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THE use of electric discharges for the synthesis of organic compounds under possible primitive Earth conditions was initiated by Miller[1–4]. Miller obtained some amino-acids, hydroxy acids and a few other organic compounds by the prolonged action of spark discharges on mixtures consisting essentially of methane, ammonia and water. These results have been confirmed by other investigators under identical or slightly different conditions[5–10].

Further investigations on this synthesis were carried out in this laboratory with the hope of obtaining additional amino-acids and perhaps also some ultra-violet-absorbing compounds.

In order to increase the probability of formation of new compounds, ethane was also included in the reaction mixtures. The use of ethane in these experiments is justifiable since the C_2 species has been detected spectroscopically in star atmospheres, comets and interstellar space[11,12]. In order to determine the over-all pattern of the compounds formed, ^{14}C-hydrocarbons, mainly ^{14}C-methane, were used as tracers. Furthermore, it was thought that the patterns obtained by autoradiography of two-dimensional chromatograms of the products may help in establishing a correlation between these and other experiments[13–15].

The results obtained show that an appreciable number of organic compounds are formed by the action of electric discharges on the foregoing mixtures. The products obtained include glycine, alanine, aspartic acid, asparagine, isoleucine (or isoasparagine), glycinamide and possibly proline; a yellowish oil, a highly insoluble polymer, and several ultra-violet-absorbing compounds. The formation of other products which give purple, green and brown derivatives with ninhydrin, suggesting the presence of amines, amino-nitriles, amino-amides and peptides, has also been observed. The ^{14}C-patterns produced by autoradiography of two-dimensional chromatograms of

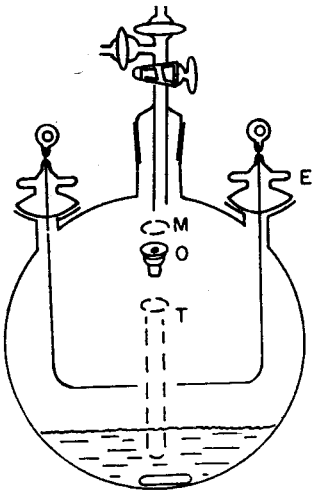


Fig. 1. Diagram of apparatus for the synthesis of organic compounds in an electric discharge. *E*, removable electrodes ; *M*, mannometer connexion ; *O*, gas-sampling orifice ; *T*, thermometer well. Dotted lines are used to represent parts on the back of the reaction vessel

the products are reasonably simple. They are not much more complex than the patterns produced by spraying the same chromatograms with ninhydrin.

Conditions of the reaction. Fig. 1 shows the design of the apparatus used, which consists of a 3-l. flask provided with removable tungsten electrodes, and with inlets and outlets for reactants and products. Temperature and pressure of the system were measured by means of a thermometer and a vacuum gauge, respectively. The liquid phase was agitated by means of a magnetic stirrer. The spark gap of the electrodes was usually 1·5 cm; but in later experiments it was increased to 3 cm. The current was supplied by a transformer (Thordarson Electric Manufacturing Co.: V.P. 110, Sec. 25,000, V × A 1,000, cyclo 50–60) from an X-ray apparatus connected to a 110-V line through a 'Variac' which was used to regulate the voltage. The discharge voltage was approximately 10,000 V when the spark gap was 1·5 cm and 15,000 V when the electrodes were separated 3 cm.

After complete evacuation of the apparatus, 300 ml. of boiled distilled water were admitted into it. Then, methane, ethane and concentrated ammonium hydroxide (15 M) were allowed into the system. Pressure readings were obtained after the introduction of each component. Whenever ^{14}C-hydrocarbons (1 mc. or less) were used, they were admitted into the evacuated apparatus before anything else (water, non-radioactive hydrocarbons and ammonium hydroxide). All the reactants used were C.P.

reagents. Care was exercised to prevent any infiltration of air into the system. Apart from this, no special treatment was followed to eliminate traces of air possibly present in the reagents. Table 1 gives the results for each experiment.

Course of the reaction. The reaction time was only 7 h or less, instead of the usual one week. This was done, in part, to make possible the detection of some of the presumed amino-acid intermediates such as amino-nitriles and amino-amides, and in part, to have reaction times comparable with those of similar experiments carried out with high-energy electrons[13–15].

The course of the reaction in the gas phase was followed by measuring the increase with time of the pressure of the system (Fig. 2). It can be seen that under the conditions used, the increase in pressure levels off after 7 h or less, depending on the concentration of the reactants. The temperature oscillation between the start and end of the experiment was only 2° or 3°, usually from 27° to 30° C. and the pressure values were not corrected for the resulting small variations in pressure.

By comparison of different experiments it can be seen that the curves are quite reproducible, and their shape is mainly determined, as might have been expected, by the initial reactant concentration in the gas phase and by the energy put into the system (spark gap). Analyses of the gas phase were not made, and therefore the nature of the gases responsible for the increased pressure was not determined. However, on the basis of previous results and knowing that dehydrogenation takes place with electric discharges, it is considered that hydrogen was one of the main gases formed. Thus, the levelling off would simply indicate that equilibrium of the dehydrogenation reaction in the gas phase at a given discharge voltage had been reached. By increasing this voltage the equilibrium

Table 1. Composition of Gas Mixtures and Other Data of the Experiments with Electric Discharges

	Exp. No.						
	S–1	*S*–2	*S*–3	*S*–4	*S*–5	*S*–6	*S*–7
CH_4 pressure (cm Hg)	12·7	7·6	10·1	10·1	7·6	10·6	22·8
$^{14}CH_4$ activity (μc.)	—	—	—	—	960	660	—
C_2H_6 pressure (cm Hg)	12·7	7·6	10·1	10·6	7·6	(31·2*)	—
H_2O (ml. liquid)	310	300	346	346	300	346	392
NH_4OH (moles/l.)	0·16	1·1	2·0	2·0	2·2	2·0	3·3
Average temperature (°C)	30	30	30	28	28	28	28
Duration of discharge (h)	1	6	5	5	7	5	5
Spark gap (cm)	1·5	1·5	1·5	1·5	1·5–3	3	3
Weight of residue (mg)	7	40	77	73	50	78	130
Activity of residue (μc.)					36	22	
Activity of distillate (μc.)					260	100	
Conversion of ^{14}C-methane to non-volatile products (per cent)					3·7	3·0	
Conversion of ^{14}C-methane to volatile water-soluble products (per cent)					28	15	

*Residual gaseous products from *S*–5, containing probably a large amount of hydrogen.

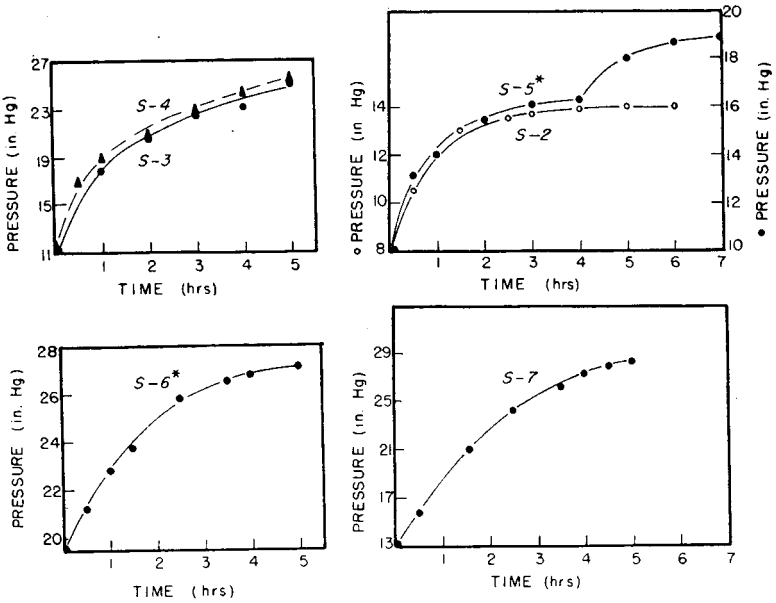


Fig. 2. Course of the reaction in the gas phase of the experiments with electric discharges The increase in pressure is supposed to be due mainly to the hydrogen formed by dehydrogenation reactions. The experiments marked with an asterisk were carried out with ^{14}C-reactants. At the fourth hour of experiment *S*–5, the spark gap was increased from 1·5 to 3 cm.

would be displaced to higher hydrogen pressures. Such a change of equilibrium can be seen in curve *S*–5 of Fig. 2.

The curves of Fig. 2 should not only give an indication of the formation of hydrogen but also of the resulting dehydrogenation products, that is, alkenes, alkynes, aldehydes, hydrogen cyanide, nitriles, hydrazine, etc., which are supposed to be precursors of organic and biochemical compounds. These curves, however, do not give any information on the processes which go on in the liquid phase. It is obvious that condensations, and mainly hydrolytic and ammonolytic reactions, will continue in the liquid phase even after the gas phase appears to have reached equilibrium.

Analysis of products. In general, the analysis was undertaken as soon as the electric discharge was discontinued. The gas phase was not analysed. The total volume of the liquid phase (about 350 ml.) was filtered and then concentrated in a vacuum rotating evaporator at 40°–45° C. When the volume had been reduced to less than 20 ml. it was transferred to a tared 50-ml. flask and the evaporation was continued to dryness. The distillate was collected in a very large trap immersed in liquid nitrogen. The distillates were set aside. The flasks with the dry residues were first weighed (Table 1) and the

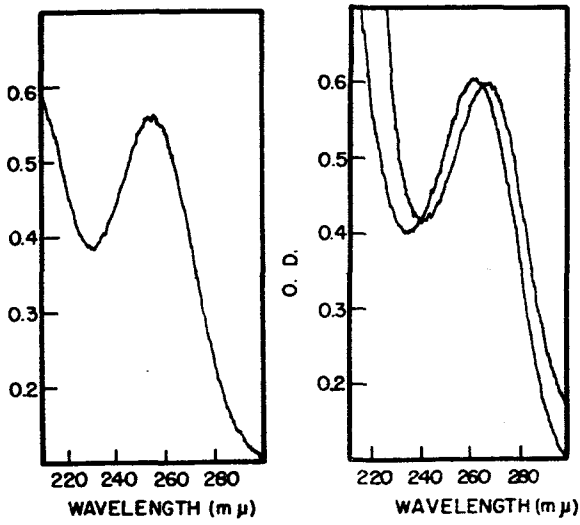


Fig. 3. Ultra-violet spectra of two compounds eluted from two-dimensional paper chromatograms of experiment *S*-3. The spectrum of *A* (left) was obtained in 1 N hydrochloric acid and the spectra of *B* (right) in 0·1 N hydrochloric acid and in 0·12 N sodium hydroxide

residues were then dissolved in 5 ml. 0·1 N hydrochloric acid. The solutions thus obtained were used in the subsequent analyses which were carried out by two-dimensional paper chromatography, ion exchange chromatography, autoradiography and spectrophotometry.

Ultra-violet-absorbing compounds. The solutions from the first three experiments, after appropriate dilution with 0·1 N hydrochloric acid, were directly examined for ultra-violet-absorbing compounds. They gave somewhat similar spectra. An aliquot of *S*-1 diluted 25 times showed a sharp absorption band at about 236 mμ (O.D. $\simeq$ 0·85). An aliquot of *S*-2 diluted 100 times and also an aliquot of *S*-3 diluted 200 times, showed a shoulder at about 236 mμ (O.D. $\simeq$ 0·6) and a broad absorption band between 250 and 300 mμ.

Aliquots of the same solutions were then analysed by two-dimensional chromatography by the ascending technique, using Whatman No. 1 paper and *n*-propanol/1 N ammonium hydroxide, 3 : 1 (PA) and *n*-butanol/acetic acid/water, 4 : 1 : 1 (BAW) as solvents. The dry chromatograms were scanned with a short wave-length (2537 Å) ultra-violet-light lamp. Two major ultra-violet-absorbing compounds were detected in the three chromatograms. One of these two compounds (*A*) had R_F 0·80 in PA and 0·40 in BAW. The other (*B*) had R_F 0·42 in PA and 0·17 in BAW. By the intensity of the spots the formation of both these compounds followed in this

quantitative order in the three experiments: S-3 > S-2 > S-1.

The areas corresponding to A and B from experiment S-3 were cut from the paper and the compounds were eluted with hydrochloric acid. Their ultra-violet spectra are shown in Fig. 3. As can be seen, compound A shows a maximum at 257 mμ and a minimum at 232 mμ. For comparison, isocytosine shows a maximum at 257 mμ and a minimum at 235 mμ at *p*H 1. Compound B shows a maximum at 262 mμ and minimum at 234 mμ in 0·1 N hydrochloric acid. This maximum shifts to 267 mμ in 0·12 N sodium hydroxide. For comparison, under the same conditions, adenine shifts from 262 to 269 mμ and purine from 261 to 273 mμ.

Although a certain similarity of compounds A and B with purines and pyrimidines is apparent, no definite statements in this respect can be made until these compounds are isolated and characterized more fully. The formation of ultra-violet-absorbing compounds in experi-

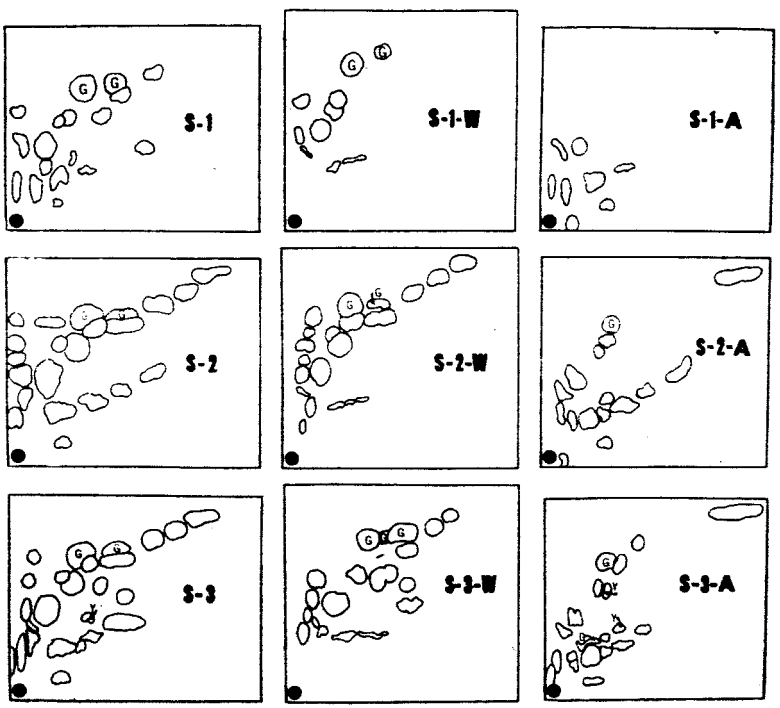


Fig. 4. Two-dimensional chromatograms (ascending) of experiments S-1, S-2, and S-3 sprayed with ninhydrin. The dark spot represents the origin. The development was first in *n*-propanol/1 N ammonium hydroxide, 3:1 (ordinate) and then in *n*-butanol/acetic acid/water, 4:1:1 (abscissa). The unlettered spots were purple or brown-purple in colour. To make chromatograms less complex the ultra-violet-absorbing spots are not shown here

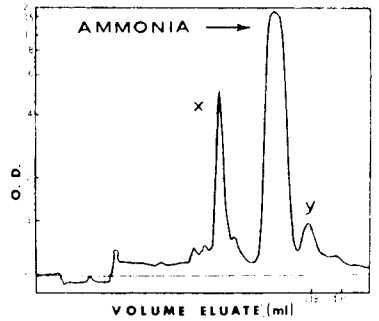
ments with electrical discharges has also been observed recently by Knight[16].

Amino-acids and other ninhydrin-positive compounds. The reaction product was next analysed for amino-acids by paper chromatography and by ion-exchange chromatography. Fig. 4 shows the reproduction of two-dimensional chromatograms (Whatman No. 3 *MM*, ascending) of *S*-1, *S*-2 and *S*-3 after spraying with ninhydrin. There are three chromatograms for each reaction product. The first corresponds to the reaction product before ion-exchange treatment, the second to the water eluate (W) from 'Dowex 2', and the third to the acid eluate (A) from the same resin. Several ninhydrin-positive compounds, which are likely amino-acids, peptides or other derivatives of amino-acids can be observed in the chromatograms of the acid eluates. At least 8 spots were observed in *S*-1-A, 16 in *S*-2-A and 20 in *S*-3-A. The ninhydrin-positive compounds of the water eluates are presumed to be amines, amino-amides and amino-nitriles. Some of the compounds in the acid or water eluates gave a green (G) or a yellow (Y) coloration with ninhydrin. Other compounds gave first a tan or yellow-brown coloration which eventually changed into purple. Some of the amides of amino-acids are known to give the foregoing colours with ninhydrin[17].

The amino-acids present in the acid eluate from experiment *S*-3 were identified by ion exchange chromatography using a Beckman–Spinco automatic analyser. (These analyses were carried out in Dr. F. H. Carpenter's laboratory, University of California, Berkeley.) The results are given in Fig. 5. The amino-acids which were identified by their positions in the eluate from a long column include aspartic acid, asparagine, glycine, alanine and isoleucine (or isoasparagine). Traces of other amino-acids can also be observed. One of these corresponds to proline by its position in the eluate and the colour given with ninhydrin.

Several unidentified peaks (*X*, *Y*, etc.) can also be observed in the eluate from the short column which is usually run for basic amino-acids. The large ammonia peak shown here is no doubt the result of hydrolysis of amino-acid amides such as asparagine.

Evidence for the formation of asparagine was also obtained in experiment *S*-7 by comparing a two-dimensional chromatogram of the reaction product of this experiment (Fig. 6) with that of a standard mixture of amino-acids containing asparagine (Fig. 7). (These chromatograms were obtained by descending development, using oxalic acid-washed Whatman No. 4 paper and *n*-propanol/15 M ammonium hydroxide/water, 6 : 3 : 1 (PAW) and *n*-butanol/propionic acid/water, 14 : 9 : 10 (BPW), as the first and second solvents, respectively). A spot with R_F 0·49 in PAW and 0·36 in



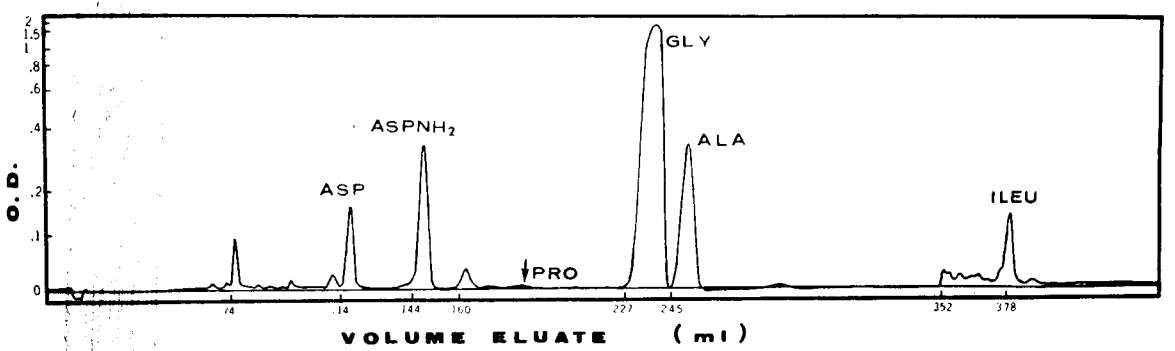


Fig. 5. Elution diagrams of the amino-acids of *S*–3–A separated by two ion exchange columns. A short column (top) was used for basic amino-acids and long one (bottom) for acidic and neutral amino-acids (Beckman-Spinco model 120 analyser)

BPW can be observed in Fig. 6. This spot showed a change in colour from brown to purple (Br → P). Authentic asparagine has R_F 0·53 in PAW and 0·39 in BPW (Fig. 7) and showed an identical change in colour (Br → P). The small differences in R_F were probably caused by the higher ionic strength of *S*-7 relative to that of the standard mixture of amino-acids.

To the right of asparagine (Fig. 6) a more intense spot which underwent the same colour change (Br → P) can be observed. By its R_F in the two solvents this compound corresponds to glycinamide. The characterization of this amide and other possible amino-amides which are suggested by the spots with similar colour changes (Br → P) in the upper right corner of the chromatogram (Fig. 6) was not carried out further because ion-exchange column chromatographic data have not yet been reported for amino-amides. It may be added that no identification of the green spots (G) of *S*-7 was attempted at this time. Tentatively these spots are presumed to be amino-amides and amino-nitriles since aspartic acid diamide[17] and β-aminopropionitrile[18] form green derivatives with ninhydrin.

The detection of asparagine and glycinamide is significant in two respects. First, it confirms earlier observations[19] made in our laboratory that the amino-amides are the immediate precursors of the amino-acids formed in these experiments. Secondly, it adds experimental

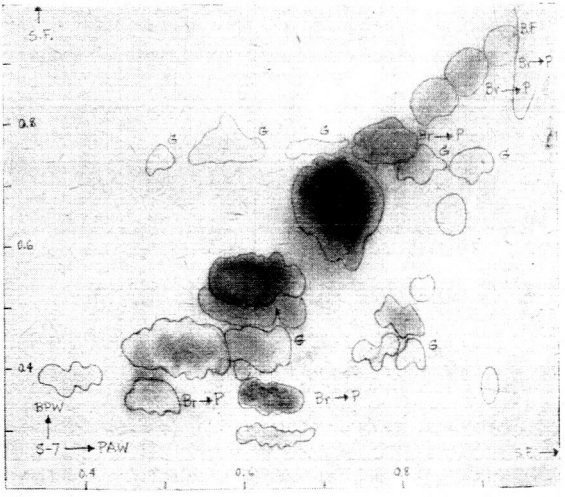


Fig. 6. Photograph of a two-dimensional paper chromatogram of *S*-7, sprayed with ninhydrin. Descending development in the BPW and PAW solvents (see text). Letters to the right or above the spots indicate colour or colour changes, That is, G, green ; Br→P, colour first brown, then turned into purple. Unlettered spots are purple

support to the hypothesis that amino-amides may have played a part in the synthesis of polypeptides under possible primitive Earth conditions[20], since it has been shown that polypeptides can be obtained from glycinamide[20] and asparagine[21] in aqueous systems.

The compound labelled as isoleucine (Fig. 5) may very well be isoasparagine, since the latter compound has an almost identical elution time to that of isoleucine in polystyrene sulphonic acid resins[22]. It should be pointed out, however, that valine, leucine and isoleucine have been identified recently in our laboratory[18] in experiments where the action of electric discharges on mixtures containing C_2 and C_3 hydrocarbons was allowed to proceed for a period of 24 h or longer. It appears that under these conditions the probability of formation of C_4 and C_5 aldehydes which are presumed to be the precursors of valine and the leucines increases significantly.

With regard to the formation of proline it should be stated that a small peak was obtained at the corresponding elution place for this compound (Fig. 5). As in the case of proline, the ninhydrin derivative of the eluted substance showed an optical density at 440; 100 per cent higher than at 570. If this peak corresponds to proline the small peak in front of proline should probably correspond to glutamic acid.

Carbon-14 compounds. Two experiments were carried out with carbon-14 reactants. In the first of these experiments (*S*-5) one millicurie of ^{14}C-methane (8 mg) was used. The unreacted ^{14}C-methane and other gaseous ^{14}C-components from *S*-5 were recovered and used in a subsequent experiment (*S*-6). This was done as follows: At the end of the experiment, the gases of the reaction product were trapped into two cold traps immersed in liquid nitrogen which were connected in series. The trap farther away from the flask contained 50 g of molecular sieve (Linde type 4*A*, 1/16-in. pellets) for the absorption of methane. In less than 1 h the pressure in the reaction flask fell to about 1 in. mercury, which is approximately the vapour pressure of water at 27° C. This indicated that essentially all the gases and volatile compounds had been condensed in the cold traps. After removing the main reaction product (yellowish solution) from the flask, the latter was evacuated and connected again to the traps, which were allowed to warm to room temperature. In this manner the bulk of the gases from the traps diffused back into the reaction flask. These gases, together with additional non-radioactive methane, ammonia and water, were used as reactants for the second experiment (*S*-6).

The concentrated reaction products from *S*-5 and *S*-6 were then individually chromatographed in the PAW–BPW solvent system described previously. Autoradiographs of these two chromatograms are shown in Figs.

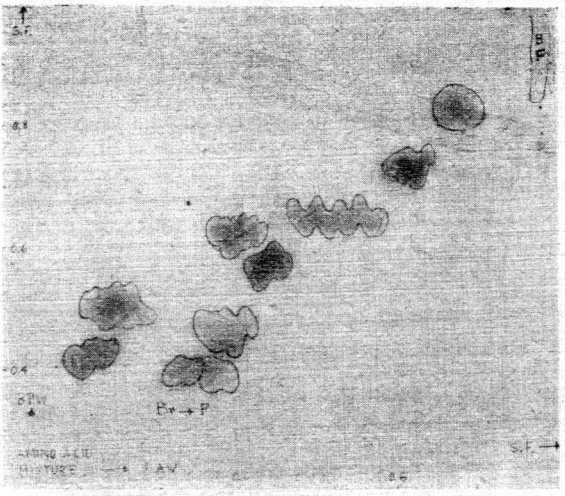


Fig. 7. Photograph of a two-dimensional chromatogram of a standard amino-acid mixture. From top to bottom following approximately the diagonal line the spots correspond to : leucine + isoleucine, valine, α-n-butyric acid, β-alanine, alanine, glycine + serine, asparagine (Br→P) and lysine. The two spots on the left correspond to glutamic acid (upper) and aspartic acid

8 and 9. By comparing the autoradiograms of S-5 and S-6 with the ninhydrin-sprayed chromatogram of S-7, a general resemblance of distribution of spots in the three chromatograms can be observed even though different methods of detection were used and the three chromatograms correspond to three different experiments.

The first three spots on the diagonal line of S-6 (Fig. 9) correspond, very likely, to asparagine, glycine and alanine, as shown by comparing this chromatogram with that of S-7 (Fig. 6) and with the chromatogram of a standard mixture of amino-acids (Fig. 7). Radioactive and ninhydrin-positive spots can also be detected in the areas corresponding to valine and the leucines. However, since no separation of bases from amphoteric substances was carried out before chromatography, some of these spots may correspond to the amides of the foregoing amino-acids, instead of the amino-acids as such. The ^{14}C-spot to the right of asparagine (Fig. 9) corresponds, most likely to glycinamide.

The largest and most diffused ninhydrin-positive compound of S-7 (Fig. 6) is probably caused by an aliphatic amine. (Aliphatic amines are known to produce diffused spots.) A radioactive spot corresponding to this compound can be observed clearly in S-5 (Fig. 8).

Aside from amino-acids, amino-amides and aliphatic amines, it is of interest that other radioactive spots appear in the area of purines and pyrimidines[23]. It should be

possible to identify these compounds by eluting them from the chromatogram and co-chromatographing them individually with the suspected authentic compounds. However, a more systematic approach would be to obtain a sample sufficiently large and submit it to analytical ion exchange chromatography. The eluate could be automatically scanned with a short wave-length ultra-violet lamp and with a radioactive scintillation counter. Coincidence of ultra-violet-absorption with radioactivity would exclude any possibility of contamination.

Polymers and other compounds. In a number of experiments a transparent solid material was observed to be formed on the glass surface of the apparatus close to the electrodes. It extended in the form of a thin layer, around each electrode, to about one-fourth of the total area of the flask.

This product was insoluble in ordinary organic solvents and water, and could not be dissolved, degraded, or hydrolysed by boiling in 6 N hydrochloric acid overnight. Only after long standing in acid could it be separated in the form of thin flakes from the glass surface. This material is presumed to be similar to that obtained by Wilson[24] in analogous experiments with electric discharges. Because of its nature, which is supposed to be a highly cross-linked polyethylene-type polymer with some functional groups, and its peculiar way of formation (surface or interphase electrodic phenomenon), it remains uncertain

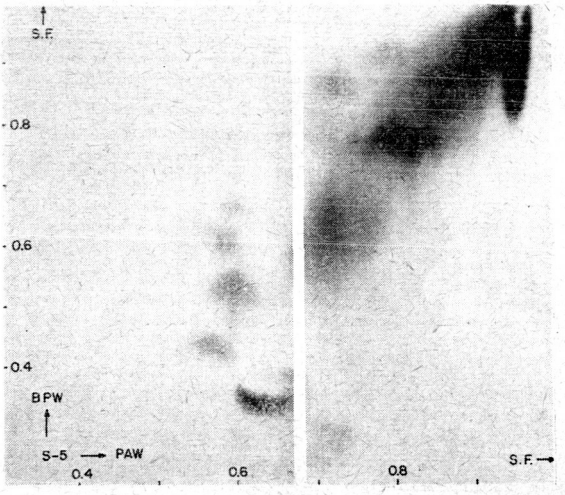


Fig. 8. Autoradiograph of a two-dimensional chromatogram of *S*–5. Because of their size this and other chromatograms had to be folded to expose two film plates which were placed back to back in the same holder. The white band corresponds exactly to the bent portion of the paper chromatogram

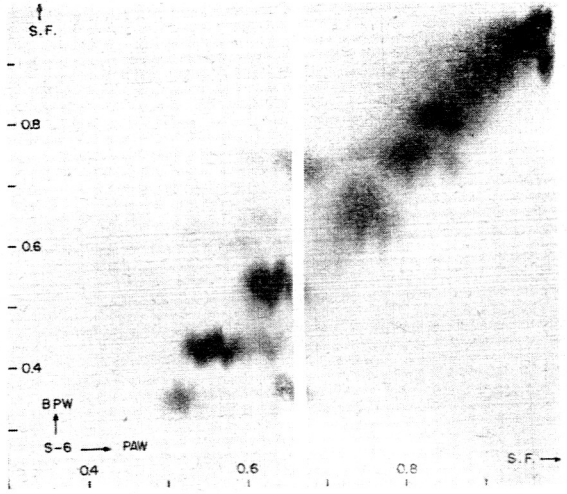


Fig. 9. Autoradiograph of a two-dimensional chromatogram of *S*-6. See Fig. 8 for explanation of white band.

at this moment the part that this or similar polymers may have played in pre-biochemical evolution.

Preliminary evidence for the formation of small-molecular-weight peptides was given by some of the two-dimensional paper chromatograms of Fig. 4. In particular *S*-3 and *S*-3-A showed two elongated spots close to the origin, which gave a brown colour on spraying with ninhydrin. This brown coloration changed very slowly into purple. Because of their low rate of migration and their characteristic way of reacting with ninhydrin, these compounds are probably peptides or polymers of amino-acids. Almost identical spots were observed in the reaction product from hydrogen cyanide–ammonia–water reaction mixtures[25], and it has been definitely shown by Lowe *et al.*[26] that polymers of amino-acids are formed in these experiments. The aforementioned ninhydrin-positive spots shown in chromatograms of *S*-3-A are supposed to correspond to the compounds *X* and *Y* which were observed to be eluted from a short ion-exchange column (Fig. 5).

Finally, it will be recalled that the gaseous and volatile products of experiments *S*-5 were condensed in two traps immersed in liquid nitrogen. After allowing the gases to diffuse back to the reaction flask, several droplets of a transparent pale yellow oil and a white viscous material were observed to remain in the trap adjacent to the flask. Both substances were radioactive and insoluble in water. The yellow oil was soluble in carbon tetrachloride. These materials were not analysed, but they suggest that the

formation of lipophilic substances is possible in experiments with electric discharges.

I thank Prof. M. Calvin for providing the stimulus and laboratory facilities to carry out these experiments, and Dr. R. Lemmon for his advice.

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